of the complexes is uncertain due to the tendency of alcohol to undergo self-association. The low $\Delta H°$ probably reflects the requirement of supplying energy to break hydrogen bonds in order to form an iodine complex. There is evidence that the relation between λ_{max} and $\Delta H°$ also is offset by steric factors.[30]

TABLE IV

SPECTROSCOPIC, DIPOLE MOMENT AND HEAT OF FORMATION DATA FOR IODINE COMPLEXES

Electron donor	λ_{max}, mμ	μ, D	$-\Delta H°$, kcal./mole
n-Heptane	520[a]		
Cyclohexane		0.0[b]	
Benzene	500[c]	0.6[b] 1.8[d]	1.3[c,e]
Toluene	497[c]		1.8[c]
p-Xylene	495[c]	0.9[b]	2.2[e]
Mesitylene	490[c]	1.1[f]	2.9[e]
1,4-Dioxane	452[g]	0.95[h]	3.5[i]
		1.3[b] 3.0[d]	
Ethyl ether	462[a]	0.7[j]	4.2[a]
Propylene oxide	460[a]		3.8[a]
Tetrahydropyran	456[a]		4.9[a]
Tetrahydrofuran	455[a]		5.3[a]
2-Methyltetrahydrofuran	455[a]		6.2[a]
Trimethylene oxide	452[a]		6.4[a]
Methanol	440[k]		1.9[k]
Ethanol	443[k]		2.1[k]3.5[l]
Pyridine 1-oxide	438[m]		5.6[m]
2-Picoline 1-oxide	437[m]		6.0[m]
3-Picoline 1-oxide	435[m]		6.1[m]
4-Picoline 1-oxide	434[m]		6.2[m]
2,6-Lutidine 1-oxide	435[m]		5.6[m]
Pyridine	417[m]	4.5[e]	7.5[m]
	422[n]	4.17[o]	7.8[n]
Triethylamine	414[p]	11.3[q] (9.3)[r]	12.0[p]

[a] This research; *n*-heptane solvent. [b] Ref. 34. [c] Ref. 10c. [d] Ref. 36; cyclohexane solvent. [e] Ref. 30a; CCl_4 solvent. [f] Ref. 38. [g] Ref. 10b,c; in pure 1,4-dioxane at slightly above 17°. [h] Ref. 35; 1,4-dioxane solvent. [i] Ref. 10b,c; *n*-hexane solvent. [j] Ref. 37. [k] Ref. 11c; CCl_4 solvent. [l] Ref. 42; *n*-hexane solvent. [m] Ref. 41; CCl_4 solvent. [n] C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954); cyclohexane solvent. [o] Ref. 35; benzene solvent. [p] S. Nagakura, THIS JOURNAL, **80**, 520 (1958). [q] Ref. 39; 1,4-dioxane solvent. [r] V. M. Kazakova and Ya. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 673 (1958); lower limit; benzene solvent.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Iodine Complexes of Some Saturated Cyclic Ethers.[1,2] II. The Ultraviolet Region

BY MILTON TAMRES AND SR. MARY BRANDON, O.P.[3]

RECEIVED MAY 1, 1959

The thermodynamic data in *n*-heptane for the complexes formed by iodine with trimethylene oxide, tetrahydrofuran-2-methyltetrahydrofuran, tetrahydropyran, propylene oxide and ethyl ether were obtained by studying the temperature dependence of the absorption spectra in the ultraviolet region. These data check very well the results reported for the visible region. Application of the Mulliken charge transfer theory to the ultraviolet spectral characteristics of the complexes implies an order of basicity of 4- > 5- > 6- > 3-membered ring, in agreement with the thermodynamic results.

Introduction

In the preceding paper[4] results were reported for a spectroscopic study of a series of cyclic ether–iodine complexes in the visible region. Since these complexes also exhibit characteristic bands in the ultraviolet region, a study of the latter region serves as an independent check in determining the strength of interaction of these electron donors with iodine. In addition, the ultraviolet spectra are of significance in their own right because the data can be interpreted in terms of charge transfer theory.[5] In this paper, the theory is applied to correlate qualitatively the spectral characteristics with the relative basicities of the ethers.

Experimental

Apparatus.—The same apparatus was used as has been described for the study in the visible region[4] with the exception of adding a hydrogen lamp and power unit (Beckman Co., Model B).

Materials.—The purification of reagents has been given previously.[4]

Procedure for Making the Solutions.—The same range of concentrations of ether in *n*-heptane (0.02 to 0.09 in mole fraction units) was used in the ultraviolet region as in the visible.[4] However, the concentration of the iodine in solution, approximately 1.5×10^{-4} mole/l., is only about one-tenth that in the visible region. This dilution, which is possible because of the much larger molar absorbancy index of the complex in the ultraviolet region, is particularly advantageous whenever there is need to reduce kinetic effects which arise from the reaction of iodine with the electron donor.

Method of Calculation.—In each study of the ether–iodine complex, the reference solution was an iodine-*n*-heptane solution of the same concentration as the iodine in the ether solution. For this case, the equation which applies is

$$\frac{1}{a_i} = \frac{1}{(a_c - a_f)K_x} \times \frac{1}{N_e} + \frac{1}{(a_c - a_f)} \qquad (1)$$

The terms have been defined previously.[4]

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept., 1956.

(2) Taken in part from the Ph.D. thesis of Sister Mary Brandon Hudson, University of Michigan, June, 1957.

(3) Department of Chemistry, Rosary College, River Forest, Illinois.

(4) Sr. M. Brandon, M. Tamres and S. Searles, Jr., THIS JOURNAL, **82**, 2129 (1960).

(5) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

Results and Discussion

Typical results obtained for the ultraviolet region are summarized in Table I. The data in Table I agree quite well with those observed in the visible region.[4] Also, because of the more dilute solutions used in the ultraviolet study, it was possible to extend to a higher temperature the investigation of the trimethylene oxide–iodine system before the onset of a side reaction.

TABLE I

SPECTROSCOPIC DATA FOR THE ULTRAVIOLET REGION OF THE IODINE–ETHER COMPLEXES[a] IN *n*-HEPTANE

Ether	λ_{max}, mμ	a_c (av.)	K_x	t^0
Trimethylene oxide	248	6800	67.6	1.0
			47.7	10.0
			36.7	15.0
2-Methyltetrahydrofuran	252	3400	35.8	10.0
			26.9	20.0
Tetrahydrofuran	249	5350	37.7	4.9
			19.6	26.0
			12.7	39.8
Tetrahydropyran	253	6200	29.1	7.0
			21.0	18.0
			16.3	25.2
			11.4	40.0
Propylene oxide	232	10950	6.4	22.2
Ethyl ether	252	5650	12.2	1.4
			9.6	9.8
			8.5	15.0

[a] For comparison to other ether–iodine complexes see ref. 9.

All the ether–iodine complexes were studied using the Beckman spectrophotometer with the exception of the complex for propylene oxide. Difficulty was encountered with this species because the spectrum of the complex appears farther out in the ultraviolet region where the complex of iodine-*n*-heptane itself becomes strongly absorbing. For propylene oxide, therefore, results were not obtained with the Beckman instrument because a zero adjustment could not be made and the one result reported was determined using the Cary spectrophotometer. Use of an iodine–*n*-heptane blank of the same iodine concentration as the ether-containing sample ensured that a maximum peak of the absorption band of this complex would be observed.

Although the ethers themselves absorb in the ultraviolet region, their molar absorbancy indices are sufficiently small at the wave length of maximum absorption of the complex so that they are not of great concern. Consequently, equation 1 still is applicable.

Scott[6] has suggested that it is preferable to evaluate the equilibrium constant of the complex using the equation

$$\frac{C_e}{(a_i - a_f)} = \frac{1}{K_c(a_e - a_f)} + \frac{C_e}{(a_e - a_f)} \qquad (2)$$

where C_e is the ether concentration in mole liter^{-1} and, hence, K_c has units of liter mole^{-1}. Except for units, this equation is essentially the same as equation 1, being obtained from it through multiplication by the concentration of ether. However, the slope and intercept are interchanged. The form of the equation will have some effect on the results determined by the method of least squares, unless all points happen to lie exactly on the line. To test any possible dependence upon the form of the equation and the choice of units, particularly the effect on the molar absorbancy indices,[2] a least squares treatment of the data was made for the following plots: (a) $1/a_i$ *vs.* $1/N_e$, (b) N_e/a_i, (c) $1/a_i$ *vs.* $1/C_e$ and (d) C_e/a_i *vs.* C_e giving K_x, K'_x and K'_c, respectively. Comparison of the results (Table II) shows no significant difference in the molar absorbancy index or in the equilibrium constant, and it must be concluded

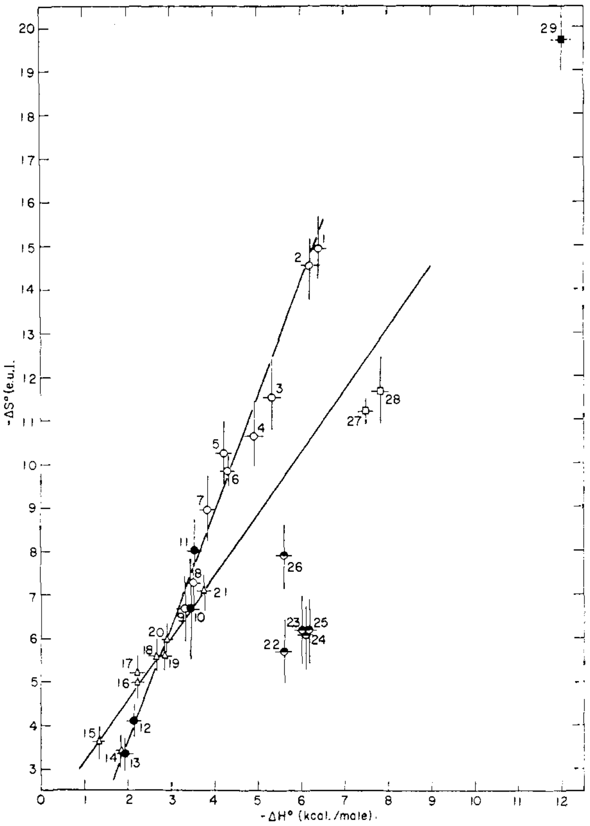

Fig. 1.—Variation of entropy of formation, $\Delta S°$, with heat of formation, $\Delta H°$, for iodine complexes in various solvents (H = *n*-heptane, C = CCl_4); ethers (○), alcohol (●), methylpyridine 1-oxides (◓), alkylbenzenes (△), pyridine (□), triethylamine (■): (1) trimethylene oxide (H), (2) 2-methyltetrahydrofuran (H), (3) tetrahydrofuran (H), (4) tetrahydropyran (H), (5) ethyl ether (H), (6) ethyl ether (C),[11] (7) propylene oxide (H), (8) 1,4-dioxane (*n*-hexane),[37b] (9) 1,4-dioxane (C),[37b] (10) *t*-butyl alcohol (C),[14] (11) ethyl alcohol (*n*-hexane),[9b] (12) ethyl alcohol (C),[11] (13) methyl alcohol (C),[11] (14) hexaethylbenzene (C),[14] (15) benzene (C),[14] (16) *p*-xylene (C),[14] (17) *sym*-tri-*t*-butylbenzene (C),[14] (18) *sym*-triethylbenzene (C),[14] (19) durene (C),[14] (20) mesitylene (C),[14] (21) hexamethylbenzene (C),[14] (22) pyridine 1-oxide (C),[10] (23) 2-picoline 1-oxide (C),[14] (24) 3-picoline 1-oxide (C),[10] (25) 4-picoline 1-oxide (C),[10] (26) 2,6-lutidine 1-oxide (C),[10] (27) pyridine (C),[10] (28) pyridine (H),[15] (29) triethylamine (H).[16] (Dotted lines represent estimated error limits in those cases where none were specified.)

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(6) R. L. Scott, *Rec. trav. chim.*, **75**, 787 (1956).

TABLE II

COMPARISON OF RESULTS OBTAINED BY USING DIFFERENT METHODS TO EVALUATE EQUILIBRIUM CONSTANTS

Ether	t, °C.	K_x	K'_x	a_c	a'_c	K_c	K'_c	a_c	a'_c
Trimethylene oxide[a]	1	67.6	69.5			10.0	10.5		
	10	47.7	49.3			7.1	7.4		
	15	36.7	38.1	6850	6770	5.5	5.7	6790	6680
2-Methyltetrahydrofuran[b]	1	56.8	55.0			8.5	8.4		
	10	37.7	37.5			5.6	5.6		
	20	27.1	28.4	850	850	4.1	4.1	850	850
Tetrahydrofuran[a,c]	4.9	37.7	44.2			6.1	6.6		
	26.0	19.6	21.9			2.9	3.3		
	39.8	12.7	14.1	5360	5170	1.8	2.2	5240	5060
Tetrahydropyran[b]	5.5	31.6	32.4						
	15.5	22.4	22.8						
	25.5	16.9	17.0						
	40.0	11.6	11.3	930	930				
Tetrahydropyran[a]	7.0	29.1	28.7			4.3	3.9		
	18.0	21.0	20.7			3.2	3.1		
	25.2	16.3	16.0			2.5	2.4		
	40.0	11.5	11.4	6180	6230	1.8	1.8	6060	6110
Propylene oxide[b]	1.0	11.9	11.2			1.9	1.8		
	9.0	9.5	9.4			1.5	1.5		
	15.0	8.7	7.9	970	995	1.3	1.3	950	940
Ethyl ether[a]	1.4	12.2	12.2			1.8	2.0		
	9.8	9.6	9.7			1.5	1.5		
	15.0	8.5	8.6	5650	5640	1.3	1.3	5480	5370

[a] Ultraviolet region. [b] Visible region, data from ref. 4. [c] In this analysis higher concentrations of ether were used than in the other studies and the method of evaluating the equilibrium constant does give somewhat different results. Generally better results were obtained when the reciprocal mole fraction of the ether was not less than ten. A very similar observation with regard to the ethyl ether–iodine system was reported by P. A. D. de Maine, ref. 11. (See Fig. 4 of that reference.)

that, for this study, the results are independent of the analytical procedure.[7]

The composite thermodynamic values ($\Delta H°$, $\Delta F°$ and $\Delta S°$) for the ether–iodine complexes have been presented in the preceding paper[8] and will not be repeated here. However, part of the data are shown in Fig. 1 in which are plotted available data of $\Delta H°$ *vs.* $\Delta S°$ for iodine complexes with oxygenated[9,10] and other electron donors. This plot is an extension of that published by de Maine[11] and shows that extrapolation of the line drawn by de Maine through the points for methanol, ethanol-*t*-butyl alcohol, ethyl ether and dioxane fits well the data obtained in this study for the ether–iodine complexes, even though a different solvent was used.[12,13] The data for the polyalkylbenzene–iodine complexes, taken from the work of Andrews and Keefer,[14] form a second line and it was concluded by de Maine[10] that the slope of the line relating $\Delta H°$ and $\Delta S°$ (or $\Delta F°$ and $\Delta H°$) seems dependent on the general classification of the donor species. The limited data for the iodine complexes with nitrogen compounds[10,15,16] do not fall on the lines,[17] at least within the error limits given. The fact that the data for pyridine 1-oxide and its methyl derivatives fall in a different region[17] signifies a need to modify de Maine's generalization for oxygenated solvents to more nearly similar species.[18]

The Ultraviolet Absorption Band.—The spectrum in the ultraviolet region which is observed with solutions containing iodine and ether must be char-

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[7] For very dilute solution, *i.e.*, $N_e \rightarrow 0$, K_x and K_c (and, of course, K'_x and K'_c) are related by the equation $K_c = K_x V_s$ where V_s is the molar volume of the solvent in units of liter mole^{-1}. Using the molar volume of *n*-heptane and the results in Table II, it may be seen that this equation holds within the limits of experimental error.

[8] Table III, ref. 4.

[9] (a) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1199 (1957), has tabulated the data for many of these complexes; (b) Y. Amako, *Sci. Repts., Tohoku Univ., First Ser.*, **40**, 147 (1956).

[10] T. Kubota, *J. Chem. Soc. Japan*, **78**, 196 (1957).

[11] P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

[12] When different solvents are used some consideration must be given to the choice of units for the equilibrium constant, whereas for a given solvent either K_c or K_x is equally suitable. For different solvents it may be best to employ K_c since no property of the solvent appears in the expression for the equilibrium constant (assuming that concentration terms rather than activity may be used). If it is assumed that the simple expression $K_c = K_x V_s$ is applicable (see ref. 7), then $\Delta F^0{}_c = \Delta F^0{}_x + RT \ln V_s$. For *n*-heptane and carbon tetrachloride, the solvents which have been employed most extensively, the molar volumes at 25° are 0.1475 and 0.0968 l./mole, respectively. Hence for *n*-heptane $\Delta F^0{}_c$ is larger than $\Delta F^0{}_x$ by 1.14 kcal./mole, while for carbon tetrachloride it is larger by 1.38 kcal./mole. This results, of course, in $\Delta S^0{}_c$ being smaller than $\Delta S^0{}_x$ by 3.8 e.u. and 4.6 e.u. for *n*-heptane and carbon tetrachloride, respectively. ΔH^0 remains essentially unaffected by the choice of units for the equilibrium constant. A plot of $\Delta S^0{}_c$ *vs.* ΔH^0 would not alter the general conclusions discussed above.

[13] The thermodynamic properties of species in solution are known to be affected by the nature of the solvent. For solvents such as *n*-heptane and carbon tetrachloride, a difference in the equilibrium constants of the iodine complexes is observed but for the complexes discussed in this paper there is no large change in ΔH^0 or ΔS^0. Recently, R. E. Merrifield and W. D. Phillips, THIS JOURNAL, **80**, 2778 (1958), pointed out that the difference due to solvent may be accounted for by considering a competition for the acid species between the donor molecule and the solvent to form a complex.

[14] L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 2164 (1955).

[15] C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

[16] S. Nagakura, *ibid.*, **80**, 520 (1958).

[17] The ΔS^0 values in Fig. 1 are based upon using K_x. Since the thermodynamic data reported in references 10, 15 and 16 are based upon K_c, they were changed[12] to a K_x basis before plotting the data.

[18] The alcohol data themselves are few and do not cover a very wide range.

acteristic of the complex since neither of the species by itself will absorb in this particular region.

A current theory, proposed by Mulliken,[5] attributes the absorption to an electronic transition from a molecular orbital of the electron donor molecule, D, to a molecular orbital of the electron acceptor molecule, A. For the ether–iodine complex this would mean that one of the lone pair electrons on the oxygen atom is transferred to an iodine molecular orbital. By making certain approximations in the Mulliken theory, as was done by Ketelaar,[19] it is possible to correlate the ultraviolet spectra with strength of interaction (or base strength). Therefore, it would seem of interest to use the theory to compare the variation of base strength with ring size.

The interaction of the ether and iodine should cause a distortion of the electron clouds of each species. It already has been pointed out[20] that iodine exhibits a dipole moment in electron donor solvents. Using Mulliken's notation,[5] the ground state of the complex may be approximated qualitatively as

$$\psi_N = a\psi_0 + b\psi_1$$

where the coefficients a and b are a measure of the magnitude of the contribution of states ψ_0 and ψ_1 to the ground state. ψ_0 is the wave function for the system in which the electron is still with the donor (*i.e.*, "no-bond" wave function, represented by DA), and ψ_1 is the wave function for the system in which the electron has been transferred from the donor to the acceptor (D^+A^-). The ratio b^2/a^2 would be a qualitative measure of the polarity of the complex. For weak interactions $a^2 >> b^2$ and, consequently, the polarity would be very low.

As was done by Ketelaar,[19] the ratio b^2/a^2 can be approximated for weakly interacting species from the experimentally determined heat of formation and the observed absorption frequency of the complex by using the relation

$$\frac{b^2}{a^2} \simeq \frac{\Delta H^0}{h\nu}$$

Results of the calculation of b^2/a^2 for the cyclic ether–iodine complexes are given in Table III. Included in this table are some results reported by Ketelaar.[19] The b^2/a^2 values for the iodine complexes of benzene, *p*-xylene and 1,4-dioxane may be compared with the dipole moment of iodine in each of these solvents which is 0.6, 0.9 and 1.3, respectively, as reported by Fairbrother.[21]

Thus it would appear that, if use of the Mulliken intermolecular charge transfer theory is valid, the ratio $\Delta H^\circ/h\nu$ (*i.e.*, b^2/a^2) may serve as a measure of relative basicity. It is interesting to note that application of this theory to the experimental results obtained in this study for the ultraviolet region would suggest that the variation of basicity with ring size for the cyclic ethers is in the order 4- > 5- > 6- > 3-membered ring.

TABLE III

POLAR CHARACTER OF THE IODINE COMPLEXES FROM HEAT OF FORMATION AND FREQUENCY OF MAXIMUM ABSORPTION OF THE CHARGE-TRANSFER SPECTRA

Compound	$-\Delta H^0$, kcal./mole	λ_{max}, mμ	$-\Delta H^0$, e.v.	$h\nu$, e.v.	b^2/a^2
Trimethylene oxide	6.4	248	0.278	5.00	0.056
2-Methyltetrahydrofuran	6.2	252	.269	4.92	.055
Tetrahydrofuran	5.3	249	.230	4.98	.046
Tetrahydropyran	4.9	253	.213	4.90	.043
Propylene oxide	3.8	232	.165	5.35	.031
Ethyl ether	4.2	252	.182	4.92	.037
Benzene[a]	1.3	296	.056	4.19	.013
Toluene[a]	1.8	302	.078	4.11	.019
p-Xylene[a]	2.0	318	.087	3.90	.022
Naphthalene[a]	1.8	360	.078	3.45	.023
1,4-Dioxane[b]	3.5	264	.152	4.69	.032

[a] Ref. 19. Due to an error in transcription, the values of ΔH^1 (in e.v.) reported by Ketelaar differ from those in this table by a factor of 0.765 in the conversion of kcal./mole to e.v. (private communication with Prof. Ketelaar). [b] Calculated from the data in ref. 19.

It must be kept in mind that some of the approximations which are made above may be rather severe. Considering the case of the ethyl ether–iodine complex, it is possible to use experimental data and theory to obtain unique values for the quantities a, b, a^*, b^* and S from the five simultaneous equations (see ref. 5 and 19 for some of the details regarding individual equations)

$$a^2 = 2abS + b^2 = 1$$

$$a^{*2} - 2a^*b^*S + b^{*2} = 1$$

$$(a^*b - ab^*) = -(aa^* - bb^*)S$$

$$\Delta H^0 = \frac{b^2}{a^2}(W_1 - W_0)$$

$$h\nu = (W_1 - W_0)\left[1 + \frac{b^2}{a^2} + \frac{b^{*2}}{a^{*2}}\right]$$

If $a^2 >> b^2$ and $a^{*2} >> b^{*2}$, the last two equations reduce to the previously considered result, $b^2/a^2 \simeq \Delta H^\circ/h\nu$. Knowledge of ΔH° and $h\nu$, and an estimate of $W_1 - W_0$ permits obtaining the unique solution.

ΔH° and $h\nu$ for the ethyl ether–iodine complex seem well established, namely, $-\Delta H^\circ = 0.18$ e.v. and $h\nu = 4.92$ e.v. However, the data for $W_1 - W_0$ are much less certain. $W_1 - W_0$ is the energy required to transfer an electron from the donor to the acceptor molecule

$$W_1 - W_0 = I_p - E_a - \frac{e^2}{r}$$

where I_p is the ionization potential of the donor, E_a is the electron affinity of the acceptor, and e^2/r is the coulombic energy of attraction of oppositely charged species at internuclear distance r. The ionization potential of ethyl ether has been reported[22] as 10.2 e.v. The electron affinity of the iodine molecule has been estimated by Mulliken[5,23] as 1.8 e.v.[24] Following the Mulliken scheme, the internuclear distance between the ether and iodine in the complex can be approximated from the sum of the van der Waals radii for oxygen and for iodine, minus an allowance for shortening due to interac-

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(19) J. A. A. Ketelaar, *J. phys. radium*, **15**, 197 (1954).

(20) See Table IV of ref. 4.

(21) (a) F. Fairbrother, *Nature*, **160** 87 (1947); (b) *J. Chem. Soc.*, 1051 (1948).

(22) T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 372 (1941); W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(23) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950), footnote 25.

(24) Mulliken actually used 1.2 e.v. for reasons stated in footnote 26 of ref. 5.

tion. The van der Waals radii for O and for I have been listed by Pauling[25] as 1.40 and 2.15 Å., respectively. Mulliken preferred using the radius of 1.8 Å. for I, the value cited by Rees.[26] However, the O–I distance derived from the Pauling table can be made to match that derived from the Rees table simply by applying a slightly larger estimate for the shortening due to interaction.[27]

In view of these difficulties, calculations were made for several estimates of $W_1 - W_0$, with the value of 4.2 e.v. being a probable upper limit and that of 3.2 e.v. being a probable lower limit. Solving the five simultaneous equations for a, b, a^*, b^* and S results in the data listed in Table IV. These values are then used to calculate the dipole moment,[28] μ_N, for the ethyl ether–iodine complex, and is given in the last column of Table IV. A comparison of the calculated with experimental value can be made using the data of Higasi[29] who reported an apparent dipole moment at 20° of 0.7 D for iodine in ethyl ether. At this temperature the iodine in pure ethyl ether is only about 88% in the form of complex. Correcting to 100% association and adding to the dipole moment of ethyl ether vapor[30] (1.16 D) gives approximately 1.9 D. Considering the approximations involved, the agreement between theory and experiment is satisfactory.[31]

TABLE IV

WAVE FUNCTION COEFFICIENTS, OVERLAP INTEGRAL AND DIPOLE MOMENT FOR THE DIETHYL ETHER-IODINE COMPLEX

$W_1 - W_0$, e.v.	a	b	a^*	b^*	S	μ_N[a] Debye
4.2	0.95	0.20	0.99	0.36	0.16	2.1
4.0	.93	.20	1.01	.43	.24	2.3
3.8	.92	.20	1.04	.51	.31	2.4
3.6	.90	.20	1.07	.60	.39	2.6
3.4	.89	.20	1.11	.70	.46	2.8
3.2	.87	.21	1.18	.82	.55	3.1

[a] Assuming an O–I internuclear distance of 3.0 Å.

If the same method is applied to the benzene–iodine complex with $I_p = 9.24$ e.v., $E_a = 1.2$ e.v. and $r = 3.4$ Å., as used by Mulliken,[5] the results are[32]: $a = 0.97$, $b = 0.12$, $a^* = 1.02$, $b^* = 0.34$ and $S = 0.22$. The calculated dipole moment of the benzene–iodine complex is $\mu_N = 0.64\ D$. This result may be compared to the experimental value of 0.6 D reported by Fairbrother which when corrected[5] to 100% complex is approximately 0.7 D. Again, the agreement is satisfactory.

For the triethylamine–iodine system, spectral data for the complex,[16] the N–I interatomic distance,[33] and the dipole moment of the complex[34,35] are known. Calculation could be applied if it were assumed that the ionization potential of triethylamine is close to that of trimethylamine.[16,36] It was found, however, that for this very strong interaction the treatment was not satisfactory.

Several investigators[37] have proposed relations between the ionization potential of the donor and the frequency of the ultraviolet absorption of the complex. The relations could be used to estimate the ionization potentials of the cyclic ethers,[38] and these can be used in turn to calculate the dipole moments[39] of the cyclic ether–iodine complexes. However, in view of the uncertainties in estimating ionization potentials from spectral data, recently discussed by Nagakura,[13] this aspect was not undertaken.

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(25) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940, p. 189.

(26) A. L. G. Rees, *J. Chem. Phys.*, **16**, 995 (1948).

(27) That the shortening may be appreciable is suggested in the work of O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 873 (1954), on the bromine–dioxane complex in the solid state where the observed O–Br distance of 2.71 Å. is considerably shorter than the sum of the van der Waals radii for bromine (1.95 Å.) and oxygen (1.40 Å.) as given by Pauling,[25] and still appreciably shorter than the sum for bromine (1.67 Å.) and oxygen (1.42 Å.) as given by Rees.[26] The shortening is less for the benzene–bromine complex, but still noticeable, the ring–Br distance being 3.36 Å. for the solid.[33]

(28) An extension of footnote 21, ref. 5, gives $\mu_N = (a^2 + abS)\mu_0 + (b^2 + abS)\mu_1$. Here, $\mu_1 = er + \mu_0$, where e is the electron charge, r is the O–I internuclear distance and μ_0 is the dipole moment of pure ethyl ether (1.16 D for the vapor[30]).

(29) K. Higasi, *J. Sci. Research Inst.* (*Tokyo*), **24**, 57 (1934).

(30) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 298.

(31) Actually, Higasi's value of 0.7 D seems low when compared to the results reported for the apparent dipole moment of iodine in 1,4-dioxane: 1.3 D [ref. 21]; 0.95 D [Ya. K. Syrkin and K. M. Amisimova, *Doklady Akad. Nauk S.S.S.R.*, **59**, 1457 (1948)]; 3.0 D [G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953)]. Higasi noted that his solution was slightly conductive, making the result of 0.7 D somewhat doubtful. The data of Kazakova and Syrkin[35] favor a higher polarization of iodine in ethyl ether than in benzene.

(32) The b/a ratio obtained in this fashion is smaller than that approximated by Ferguson and Matsen [*J. Chem. Phys.*, **29**, 105 (1958)] but is closer to that given by Mulliken.[5] The latter estimated S to be about 0.1 and his results for the coefficients of the wave functions were: $a = 0.97$, $b = 0.17$, $a^* = 0.99$ and $b^* = 0.27$. The same estimate of $S \simeq 0.1$ was made for the chloranil–hexamethylbenzene complex by G. Briegleb and J. Czekalla [*Z. Elektrochem.*, **58**, 249 (1954)] in comparing the experimental oscillator strength with that calculated from charge transfer theory. The overlap integral might be expected to be slightly greater for this complex than for benzene–iodine because the latter complex is somewhat weaker [R. E. Merrifield and W. D. Phillips, THIS JOURNAL, **80**, 2778 (1958)].

(33) O. Hassel, *Mol. Phys.*, **1**, 241 (1958), for the solid.

(34) H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

(35) V. M. Kazakova and Ya. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 673 (1958).

(36) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(37) (a) S. H. Hastings, J. L. Franklin, J. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953); (b) C. van de Stolpe, Ph.D. thesis, Amsterdam, 1953; (c) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(38) The ionization potentials would be very close except, perhaps, for propylene oxide.

(39) Dipole moment data for the cyclic ethers are in ref. 30, p. 299.